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REGULAR ARTICLE

Thirty years of relativistic self-consistent field theory for molecules: relativistic and electron correlation effects for atomic and molecular systems of transactinide superheavy elements up to ekaplutonium E126 with g-atomic spinors in the ground state configuration

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Abstract Relativistic Hartree–Fock–Roothaan (RHFR) self-consistent field theory for molecules developed by Malli and Oreg (J Chem Phys **63**, 830, 1975) is reviewed. Ab initio all-electron fully relativistic Dirac–Fock and the corresponding nonrelativistic Hartree–Fock calculations for a number of molecular systems of heavy and superheavy elements are discussed in order to asecrtain relativistic effects. It is pointed out for the first time that there are dramatic *antibinding effects* of relativity for diatomics of the superheavy elements ekagold and ekaastatine. These are *first* results of *antibinding effects* of relativity in relativistic quantum chemistry. Moreover, in order to take into account the relativistic and electron correlation effects *simultaneously* for these systems, relativistic Moeller Plesset second order (RMP2), coupled-cluster singles doubles (RCCSD) and RCCSD with inclusion of triple corrections perturbationally (RCCSD(T)) calculations performed by the author for a number of atomic and molecular systems of superheavy elements (SHE) including the primordial SHE ekaplutonium E126 ($Z = 126$) (with g atomic spinors occupied in the ground state atomic configuration) are reported. Such calculations and results have not been reported before for systems of superheavy elements.

In memoriam

This paper is dedicated to the memory of Prof. Serafin Fraga, whom I first met more than 45 years ago in June 1960 when we both were in Prof. R. S. Mulliken's Laboratory at The University of Chicago, USA. Dr. Fraga left Chicago in 1961 for a faculty position at University of Alberta, Canada and remained there until his last days. In May 1965 I left Department of Physcis, Yale university, New Haven, USA. and I also moved to University of Alberta, Canada to work in Theoretical Chemistry Division where I was very happy to meet Prof. Fraga after a gap of about 4 years. He and his family offered me a warm welcome and generous hospitality. Prof. Fraga kindly invited me to join him to work on the calculation of physical properties of many-electron systems. We published jointly more than a dozen research papers and in addition co-authored the classical work *Many-electron System*: *Properties and Interactions* by S. Fraga and G. Malli, W. B. Saunders, Philadelphia (1968). I would like to mention that Prof. Fraga alone was invited to write the above-mentioned monograph; however, out of generosity he insisted that I be the co-author despite my protests that I would not be able to do justice to this monograph as I was at an early stage of my academic career. Prof. Fraga, however, prevailed and I gave in and I learned a lot from him about the crucial details which should be carefully looked into while writing a book. Needless to say Prof. Fraga worked extremely hard and we the youngsters were amazed at his extraordinary capacity to work concurrently at various research topics. Prof. Fraga in his early days of research worked mostly in the application of quantum mechanics to problems in atomic and molecular physics; however, he later moved on to Quantum Biology and Immunology and he made very seminal contributions to a wide variety of subjects like protein structure, molecular recognition, synthetic vaccines etc. In 1966, I left Edmonton and moved to Simon Fraser University, Burnaby, Canada where I have remained ever since. Prof. Fraga and I remained in touch for many years after I left Edmonton and we had most cordial relations. I valued his

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Contribution to the Serafin Fraga Memorial Issue.

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mature advice and sagacious wisdom. Prof. Fraga was a prolific and dedicated researcher for about half a century and two of his earliest areas of pioneering theoretical research were *nonrelativistic SCF theory* (Fraga in Theor Chim Acta 2: 403, 406, 411, 416, 1964) and *Electronic structure of the Transactinides with $6d^N 7s^2$, $7p^N$ and $8s^N$ Configurations* [Fraga in Anales de Fisica (Madrid), 70:249, 1973]. In the latter paper he used the numerical Hartree–Fock method to calculate the ground and excited states of the neutral atoms and positive ions of transactinide elements (with nuclear charges Z from 103 to 120). It is remarkable that more than 3 decades ago Prof. Fraga was able to perform successfully HF calculations on open-shell transactinides atomic systems. Since my own research in relativistic quantum chemistry especially during the last 3 decades has focused upon the *Relativistic self- consistent field theory* and *electronic structure and bonding of molecular systems of heavy actinide and transactinide superheavy elements (SHE*), I hope that my paper in this issue of Theoretical Chemistry Accounts would constitute a fitting contribution to the memory of Prof. Fraga who was one of the pioneers who made fundamental contributions to nonrelativistic SCF theory as well as the calculation of electronic structure of transactinides decades ago. Prof. Fraga was a genuine friend and distinguished colleague. In his demise, theoretical chemists have lost a pioneer who put theoretical chemistry on very strong foundations. We all will sorely miss him.

1 Introduction

Theory of relativity and quantum mechanics are basic foundations of theoretical physics. Most physicists and chemists have investigated atomic and molecular structure for decades using quantum mechanics based upon Schrodinger's equation. However, Schrödinger's equation is not Lorentz invariant as it does not obey the special theory of relativity, and is labeled as nonrelativistic (NR). The behavior of fast-moving bodies, as predicted by relativity (which postulates a finite velocity of light); however, is significantly different from that predicted by nonrelativistic mechanics (which Schrödinger assumed). It was the genius of Dirac [1] who invented quantum mechanics in conformity with relativity ideas, and his approach is well-known as relativistic quantum mechanics (RQM). It is clear, that nonrelativistic quantum mechanics (NRQM) would be inappropriate for investigating the behavior of electrons in atomic and molecular systems if the electrons in these systems moved at speeds comparable to that of light. The simple Bohr model of one-electron atomic system with nuclear charge Z predicts that this will happen for an atomic system with $Z \sim 70$. Therefore a priori it would be more appropriate to use relativistic quantum mechanics (RQM) for an understanding of the electronic structure of atoms and molecules of heavy (with $75 < Z > 102$) and especially transactinide or superheavy elements (SHE) with $Z > 103$ in which electrons move at very high speeds.

The chemistry and physics of the man-made SHE have been vigorously investigated both experimentally and theoretically [2–25]. It is well-known [10–25] that relativistic effects are expected to be very large in the transactinide chemistry (TAC) and that dynamics of even the valence electrons of the atoms of the transactinide elements would be significantly affected by relativity so that extrapolation of chemical properties of these heaviest elements from their lighter homologs, may no longer be valid. Moreover, due to both the direct and indirect relativistic effects [11–21] electron configuration of some superheavy elements may turn out to be different from what would be expected from their position in the periodic table. It is obvious that the consequences of pronounced relativistic effects would be clearly manifested in the chemistry and physics of heavy and especially SHE.

2 Relativistic SCF treatment for many-electron atoms

A generalization of Dirac's relativistic equation for an electron is mandatory in order to study many-electron systems of heavy and superheavy elements. Breit [26] attempted to extend Dirac's equation to two electrons for which he incorporated from classical considerations the magnetic and retardation terms in addition to the nonrelativistic electron–electron Coulomb interaction; however, the resulting equation was not Lorentz invariant. In 1935, Swirles [27] developed relativistic self-consistent field formalism for many electron closed-shell *atoms*. She took the total N-electron Hamiltonian to consist of N Dirac one-electron terms plus the interelectron coulomb pair interactions, which is the so-called Dirac-Coulomb (DC) Hamiltonian for N-electrons atomic systems. She invoked the variational principle (without worrying about the *unboundedness* of the Dirac's operator) and derived relativistic atomic self-consistent field equations following the norelativistic HF treatment. Her treatment was quite complex and cumbersome; which she applied to the helium atom neglecting the complicated *exchange terms* which were very difficult to evaluate even for He. In 1961 Grant [28] reformulated the relativistic self consistent field (SCF) theory using algebra of tensor operators and obtained expressions for the numerical relativistic Hartree–Fock [also called Dirac-Fock (DF)] equations for closed-shell atomic systems. In 1967 Coulthard [29], published the results of his DF calculation with full details of the total relativistic and spinor energies for Hg.

During the late 1960s, relativistic numerical atomic calculations were reported by numerous workers under various approximations for heavy and superheavy atoms [30–33], and an extensive account of the various relativistic atomic calculations can be found in Grant [34]. In 1973, Desclaux [35] published the results of most extensive numerical DF calculations for all atoms with $Z = 1$–120. This monumental publication lists for each atomic configuration the total DF energy, the magnetic energy (the first term of Breit's opearator), spinor energies, nonrelativistic limit energy, radial expectation values, ratio of the relativistic to norelativistic values for the atomic radius, etc. The exhaustive results reported by Desclaux [35] have been known for decades for their accuracy; the only *error* found in Desclaux [35] by the present author [36] was in the total energy listed for Fr, which I believe is due to the *typing error*, since the error involved exchanging the last two digits before the decimal place.

Soon after the appearance of numerical DF calculations for Hg and other heavy atoms, attempts were made to extend Roothaan's [37] finite basis set expansion method to develop a relativistic Hartree–Fock–Roothaan (RHFR) formalism for atoms. The early attempts [38,39] however, were purely formal and no relativistic atomic calculations were attempted. The *first* RHFR SCF formalism for *closed-shell* atoms was developed in 1967 by Kim [40], a student of Roothaan. Kim [40] also developed the first computer code for RHFR SCF atomic calculations and reported results for the closed-shell atoms He, Be and Ne. Moreover, Kim was the first to treat the full Breit interaction (*magnetic* and *retardation terms*) and he reported results of the contribution of the Breit interaction evaluated using first-order perturbation theory with the RHFR SCF wavefunction as the unperturbed wavefunction.Thus the stage was set for RHFR calculations for many-electron atoms; however, Kim [40] was quite pessimistic and he stressed that (i) extension of his closed-shell treatment to *general open-shell* atomic configurations would require a considerable amount of work on the theory of angular momentum coupling, (ii) the outlook for application of his RHFR method to *large atoms* ($Z > 50$) or *molecules* was not bright because the computers available were too slow and short on memory storage to handle the large number of basis functions needed to represent the RHFR solutions to an accuracy which makes any relativistic calculation meaningful. However both these challenges were met within the next decade. Kagawa [41] extended the RHFR treatment of Kim [40] to a number of atomic open-shells and reported the results of his RHFR calculations for the first row transition atoms Sc to Cu with d^n open-shell configurations.

In 1975 Malli and Oreg [42] developed the *first* relativistic RHFR formalism for molecules, which we briefly outline in the next section.

3 Relativistic self-consistent field theory for molecules: LCAS/MS Dirac–Fock (–Breit) SCF treatment of Malli and Oreg for molecules

We present here only a brief account of the RHFR matrix formalism for molecules *first* developed by Malli and Oreg [42] in 1975 within the molecular spinor (MS) as a linear combination of atomic spinors (LCAS) i.e. the LCAS/MS approximation in close analogy to the well-known LCAO/MO Hartree–Fock matrix formulation of Roothaan [37]. We refer the reader to the original paper [42] for details, however bare essentials can be found in various abridged accounts [14–16,21].

The *approximate* relativistic Dirac–Coulomb Hamiltonian ($\mathrm{H_{DC}}$) for an N-electron molecular system containing n nuclei, under the Born–Oppenheimer approximation (omitting the nuclear repulsion terms which are constant for a given molecular configuration) is taken to be of the form (in atomic units, au):

$$\mathrm{H_{DC}} = \sum_{i=1}^{N} \mathrm{H_D}(i) + \sum_{i<j} \frac{1}{r_{ij}} \tag{1}$$

In Eq. (1), the $\mathrm{H_D}(i)$ consists of the Dirac's kinetic energy operator, mass energy and nuclear attraction of the ith electron and has the well-known expression, viz.;

$$\mathrm{H_D}(i) = c\alpha_i \cdot \mathrm{p}_i + (\beta_i - 1)c^2 + V_{\mathrm{nuc}}, \tag{2}$$

where the Dirac's matrix operators α and β have the usual 4×4 matrix representation [42].

The rest mass energy of an electron has been subtracted in Eq. (2), in order to get its binding energy, and the potential V_{nuc} due to *n finite nuclei* of the molecular system is taken to be the sum of their nuclear potentials viz.;$V_{\mathrm{nuc}} = \sum_n V_n$, and for molecular systems involving heavy atoms (with $Z > 70$), finite nuclear model is invariably used. We shall use the Gaussian nuclear model in which a single Gaussian function is used for each nuclear charge distribution. The advantage of using this nuclear model in basis set calculations for polyatomics (with finite nuclei) is due to the fact that all the multi-centre nuclear attraction and inter-electron repulsion integrals can be calculated analytically in a straightforward way. The instantaneous Coulomb repulsion between the electrons is treated *nonrelativistically* in the Dirac–Coulomb Hamiltonian and the magnetic and retardation corrections to it are generally included perturbationally as discussed later.

The N-electron wavefunction Φ for the closed-shell molecular system is taken as a single Slater determinant (SD), also called an antisymmetrized product (AP) of one-electron four-component molecular spinors (MS) [22],viz.

$$\Phi = (N!)^{-1/2} \mid \phi_1(1)\phi_2(2)\phi_3(3)\cdots\phi_N(N) \mid . \tag{3}$$

The molecular spinors (MS) ϕ_i are usually taken to form an orthonormal set and can be constructed so as to transform like the *extra* or *additional irreducible representations* (EIR) of the double symmetry group of the molecule under investigation [55,56]. The energy expectation value E can then be written as

$$E = \langle \Phi \mid \mathrm{H} \mid \Phi \rangle / \langle \Phi \mid \Phi \rangle \tag{4}$$

The molecular spinors ϕ_i are expressed in terms of the *large* and *small* components:

$$\phi_i^X = \sum_{q=1}^{n} C_{iq}^X \chi_q^X, \quad X = \mathrm{L} \text{ or } \mathrm{S}. \tag{5}$$

The χ_q^L and the ϕ_i can be symmetry adapted; however, we shall ignore the double group symmetry labels for the spinors. The basis spinors χ_q^X will, however, be constrained to obey the kinetic balance relation [57], viz.

$$\chi_q^\mathrm{S} = (\sigma \cdot p)\chi_q^\mathrm{L}. \tag{6}$$

Then following Malli and Oreg [42], the Dirac–Hartree–Fock–Roothaan (DHFR) or RHFR SCF equations for *closed-shell* molecules can be written as

$$\mathbf{F}\mathrm{c}_i = \varepsilon_i \mathbf{s}\mathrm{c}_i, \tag{7}$$

where in Eq. (7), F is the Dirac–Fock matrix operator, the ε_i is the orbital energy of the molecular spinor (MS) ϕ_i and S is the overlap matrix.

It was shown by Malli and Oreg [42] that all the matrix elements occurring in RHFR SCF calculations for polyatomics in general can be expressed [42] in terms of the types of matrix elements which arise in nonrelativistic HFR SCF calculations for polyatomic molecules, and well-developed techniques for the evaluation of these matrix elements using Gaussian type functions as the basis set have been in existence for decades.

The electron–electron Coulomb interaction is treated *nonrelativistically* in H_{DC} as mentioned earlier in this section. The Breit [26] interaction consisting of the magnetic and retardation terms was proposed to remedy partially this defect of H_DC, and the addition of Breit interaction (B_{ij}) to H_{DC} leads to the Dirac–Coulomb–Breit (DCB) Hamiltonian H_DCB, which has the form

$$\mathrm{H}_\mathrm{DCB} = \mathrm{H}_\mathrm{DC} + \sum_{i<j} \mathrm{B}_{ij}. \tag{8}$$

The B_{ij} in Eq. (8) is usually written as

$$\mathrm{B}_{ij} = -\frac{1}{2}\{(\alpha_i \cdot \alpha_j)\mathrm{r}_{ij}^{-1} + (\alpha_\mathrm{i} \cdot \mathrm{r}_{ij})(\alpha_j \cdot \mathrm{r}_{ij})\mathrm{r}_{ij}^{-3}\}. \tag{9}$$

Twice the first term in Eq. (9) called the magnetic or Gaunt interaction is the dominant part of Breit interaction; the retardation term is about 10% of the Gaunt interaction and in general the contribution of Breit interaction is fairly marginal compared to the Coulomb interaction term. The use of H_DCB as the starting point for variational molecular calculations leads to the DFB SCF equations The DFB matrix operator occurring in the DFB SCF equations, involves the matrix elements of the magnetic and retardation interactions. The expressions for the matrix elements of the magnetic or Gaunt interaction for molecules in general are given in Malli and Oreg [42] and the Gaunt interaction has been included in recent relativistic molecular DFB SCF calculations as well as perturbationally [22], with H_DC as the unperturbed Hamiltonian. The retardation term, however, has not been included so far in general for relativistic molecular calculations. It should be pointed out that as in the NR HF SCF theory, electron correlation effects are not included in the relativistic DF treatment for atoms and molecules. A very useful approach to include simultaneously both the relativistic and electron correlation effects is the coupled-cluster approach which we outline briefly in the next section.

4 Relativistic coupled-cluster methodology

The coupled-cluster (CC) method [43–48] has emerged as a very powerful tool for calculating the *correlation effects* in atomic and molecular systems, as it includes electron correlation to high order and is *size extensive*, a property of particular importance for heavy systems, for which relativistic effects are also very significant. In order to treat both the relativistic and electron correlation effects *simultaneously*, the relativistic coupled-cluster (RCC) has been developed [49] by interfacing the relativistic DF (Breit) SCF theory with the CC method. The RCC method and its recent applications to atomic and molecular systems [49–51] are summarized below.

Although the relativistic many-body Hamiltonian for atomic and molecular systems cannot be expressed in closed potential form; nonetheless the nonrelativistic many-body formalism can be extended to the relativistic domain by employing the formalism based on effective potentials and derived with arbitrary accuracy from quantum electrodynamics (QED) as described by Lindgren [52]. The transition from the nonrelativistic to the fully relativistic case requires two major modifications: (1) two-component Pauli–Schrodinger *spinorbitals* are replaced by *four-componen*t Dirac *spinors*, (2) instantaneous electron-electron coulomb interactions are supplanted by the irreducible multiphoton interactions along with the radiative and renormalization counter terms.

The starting point for the RCC method (with single and double excitations) which includes relativistic and electron correlation effects simultaneously to high order for molecules, is the projected Dirac–Coulomb (or

Dirac–Coulomb–Breit) Hamiltonian [53]:

$$\mathrm{H}+ = \mathrm{H}_0 + V, \tag{10}$$

where

$$\mathrm{H}_0 = \sum_i \Lambda_i^+ \mathrm{H}_\mathrm{D}(i) \Lambda_i^+ \tag{11}$$

$$\mathrm{H}_\mathrm{D}(i) = c\alpha_i \cdot p_i + c^2(\beta_i - 1) + V_\mathrm{nuc}(i) + U(i) \tag{12}$$

and

$$V = \sum_{i<j} \Lambda_i^+ \Lambda_j^+ (V_\mathrm{eff})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+ \tag{13}$$

An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V, and this potential is chosen to approximate the effect of electron–electron interaction and it may be the DF self-consistent field potential. The $\Lambda+$ is a product of projection operators on to the positive energy states of the Dirac Hamiltonian H_D, and because of the projection operators, the Hamiltonian H+ has normalizable bound state solutions. This approximation is known as the no-(virtual)-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential V_eff depends upon the gauge used, and in the particular Coulomb gauge (in atomic units, correct to the second order in fine structure constant α) it has the form:

$$V_\mathrm{eff} = \frac{1}{r_{12}} + B_{12} + \mathrm{O}(\alpha^3), \tag{14}$$

where the B_{12} is frequency independent Breit interaction defined in Eq. (9) above.

The no-pair DCB Hamiltonian H+ may be rewritten [53], in second-quantized form in terms of normal-ordered products of the spinor operators, $\{r^+S\}$ and $\{r^+s^+ut\}$:

$$\mathrm{H} = \mathrm{H}_+ - \langle 0|\,\mathrm{H}_+\,|0\rangle = \sum_{rs} f_{rs}\{r^+s\} + \frac{1}{4}\sum_{rstu}\langle rs||tu\rangle\{r^+s^+ut\}, \tag{15}$$

where f_{rs} and $\langle rs||tu\rangle$. are elements of one-electron DF and antisymmetrized two-electron Coulomb–Breit interaction matrices over Dirac four-component spinors, respectively. The effect of the projection operators $\Lambda+$ is now taken over by the normal ordering, denoted by the curly braces in the equation above, which requires annihilation operators to be moved to the right of the creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive energy state, and the negative energy state is ignored. The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic coupled-cluster theory. The implementation of the four-component matrix DF and relativistic CC calculations is carried out by expansion of atomic or molecular spinors in basis sets of Gaussian four-component spinors. The four-component method involves generating the orbitals or spinors by Dirac–Fock calculation, followed by applying the coupled cluster scheme at the singles-and-doubles (CCSD) level. The Dirac–Fock functions and matrix elements are calculated by the MOLFDIR code [54], hereafter referred to as code. The coupled-cluster stage is more complicated in four-component case as compared with non-relativistic one or two component cases due to the appearance of complex orbitals or complex spin-orbit integrals. The full double group symmetry [55,56] is used at the Dirac–Fock level; only Abelian subgroups are considered in the RCC code [54]. Kinetic [57] and atomic balance [54] conditions are imposed on the basis to avoid variational collapse.

5 Universal Gaussian basis set for DFB and Dirac–Fock relativistic coupled-cluster calculations on atomic and molecular systems of transactinide superheavy elements

We have developed highly accurate relativistic universal Gaussian basis set (UGBS) [36,58,59] for all atoms up to ekaplutonium and have used it in all of our DFB calculations on numerous molecules of SHE with the code [54] using the Gaussian nuclear model. The UGBS was contracted using the general contraction scheme along with the atomic balance procedure as implemented in the code [54]. The UGBS for the small (S) component of the atoms used in our calculations was obtained from the UGBS of their corresponding large (L) component such that the L and S components of each atom satisfy the so-called kinetic balance condition [57]. The exponents of the L component of the UGBS used in our various calculations are given in our earlier papers cited above, and the DF SCF total energies obtained with our contracted relativistic UGBS for various atoms (using the Gaussian nuclear model) are in excellent agreement with those obtained with the numerical finite difference code.

6 Dirac–Fock–Breit calculations for molecules of superheavy transactinide elements

We have investigated hundreds of molecular systems of heavy actinide and superheavy transactinide elements, however, we shall discuss here briefly a few of our all-electron relativistic DF SCF calculations for molecules of transactinide SHE.

7 Seaborgium hexachloride

Ab initio all-electron DF and HF SCF calculations have been performed for the hexachloride and hexafluoride of Sg. The very extensive UGBS for Sg, viz.; the Sg [L: 30s 30p 18d

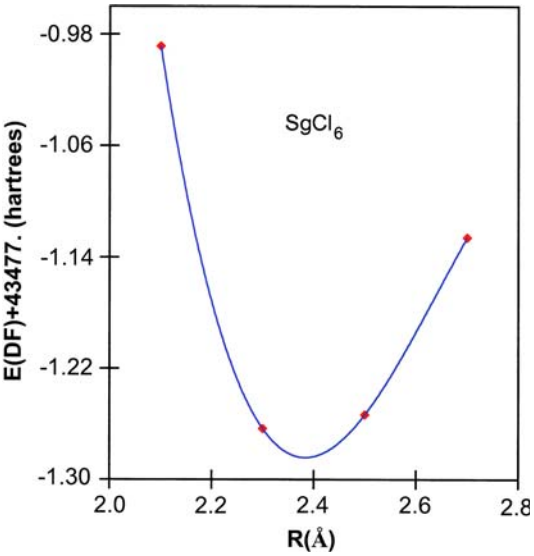

Fig. 1 Total Dirac-Fock (DF) energies for octahedral $SgCl_6$ at various Sg–Cl internuclear distances reproduced by permission from Ref. [22]

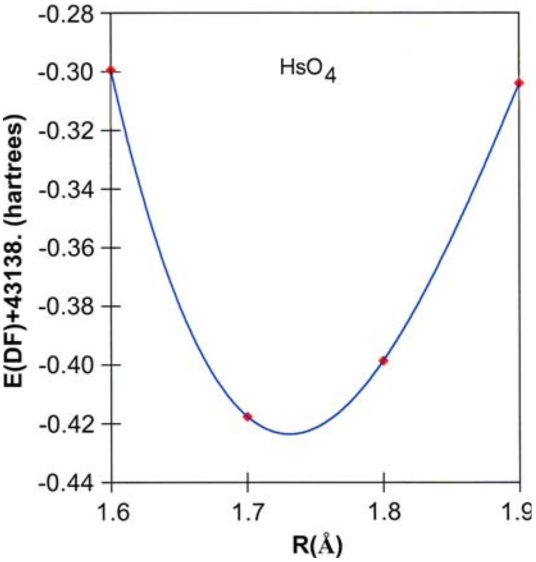

Fig. 2 Total DF energy of Hassium tetroxide (Td) at various Hs–O internuclear distances reproduced by permission from Ref. [22]

13f| S:30s 30p 30d 18f 13g] UGBS (where the L and S stand for the large and small components, respectively) contracted to Sg [L: 12s 14p 11d 6f|S: 16s 23p 22d 14f 8g] and. the contracted UGBS Cl [L: 6s 7p|S: 8s 7p 9d] were used for calculations on $SgCl_6$. We have performed DF and HF SCF calculations at four Sg–Cl bond lengths, assuming octahedral geometry for $SgCl_6$. The results were fitted to a polynomial and gave an optimized Sg–Cl bond length of 2.384 Å along with the corresponding total DF energy of −43,491.3002 au for $SgCl_6$. We predict an atomization energy (Ae) of 16.75 eV for $SgCl_6$, using the results of our DF calculations for $SgCl_6$ and the total energies of its constituent atoms. The highest occupied molecular spinor (HOMS) and the lowest unoccupied molecular spinor (LUMS) of $SgCl_6$ are calculated using the results of our DF SCF calculations at −0.4669 and −0.0885 au, respectively, which yield a HOMS-LUMS gap of 10.3 eV. However, a *fourfold decrease* was predicted for this gap in the DS SCC calculations of Pershina [20], who calculates it as 2.46 eV. In Fig. 1, we present our results for the total relativistic DF SCF energy at four Sg–Cl bond distances for $SgCl_6$. We predict that $SgCl_6$ should be quite stable and volatile enough for the experimentalists to detect it using gas chromatography.

8 Relativistic effects for the volatility and atomization energy of Hassium and Osmium tetroxides

It is well-known that the lighter homolog of Hs viz, Os forms OsO_4 a highly volatile molecular compound and it would be interesting to investigate theoretically both HsO_4 and OsO_4 so as to ascertain the effects of relativity in the electronic structure, volatility, atomization energy, etc. We have performed ab initio all-electron HF and DF SCF calculations on both these compounds assuming a tetrahedral geometry; however, the Hs–O and Os–O bond distances were optimized by performing HF and DF SCF calculations on HsO_4 and OsO_4 at four internuclear distances each and thereby eight calculations were performed for each molecule, assuming Gaussian nuclear models using atomic mass for Hs of 269. The relativistic uncontracted O [L: 18s 12p|S:12s 18p 12d] UGBS contracted to O [L: 5s 4p|S: 5s, 6p 6d] and the NR UGBS contracted to O [L: 5s 4p] were used in DF and NR HF SCF calculations, on HsO_4 and OsO_4, respectively. DF SCF calculations on the tetrahedral $(T_d)HsO_4$ were performed at four Hs–O distances and the total DF energies obtained were fitted to a polynomial leading to an optimized Hs–O bond length of 1.731 Å, with an energy minimum of −43,138.4235 au, yielding thereby an Ae of 0.5641 au or 15.35 eV. Mulliken population analysis [61] leads to a charge of 1.06 on Hs, and each O therefore has a charge of −0.265. The corresponding NR HF SCF calculations predict an atomization energy of 6.83 eV and the charges on Hs and O of 1.14 and −0.285, respectively. Our relativistic wavefunction, which predicts *twice* as much atomization energy as the NR HF wavefunction; however, predicts only a slight increase in the volatility of HsO_4. The total DF energy of HsO_4 as a function of the bond length Hs–O is depicted in Fig. 2. The DF SCF calculations for the tetrahedral OsO_4 similarly yielded an optimum value of 1.664 Å for the Os–O bond distance and energy minimum at −17570.7332 au predicting thereby an Ae of 10.32 eV. Similarly, the corresponding NR HF calculations yield an optimum bond length of 1.70 Å and an Ae of merely 5.59 eV. Therefore, the relativistic effects predict 250 and 185% *larger* atomization energy for HsO_4 and OsO_4, respectively, than that predicted with our NR HF calculations. There are therefore dramatic relativistic effects for the atomization energy of the tetroxides of Hs and Os.

9 Ab initio all-electron Dirac–Fock and Hartree–Fock calculations for molecules of ekaplutonium: $E126F_6$, $E126Cl_6$ and $E126O_6$

We have performed all-electron DF (within the NOSS approximation) and NR HF SCF calculations for $E126F_6$, $E126Cl_6$ and $E126O_6$ using our contracted UGBS for all the atoms constituting the molecules under investigation. In the DFNOSS approximation, all two-electron matrix elements involving the small component of spinors are neglected in the final SCF stage of DF SCF calculations. The relativistic uncontracted UGBS E126 [L: 32s 32p 18d 13f|S: 32s 32p 32d 18f 13g] for E126 (with $6f^6$ configuration similar to its lighter homolog Pu) contracted using the atomic and kinetic balance as implemented in the code [54] to the UGBS E126 [L: 14s 16p 12d 9f|S: 19s 26p 24d 18f 14g] was used in all relativistic calculations for involving E126 molecules. However, the nonrelativistic (NR) uncontracted UGBS E126 [L: 30s 30p 22d 16f] contracted to E126 [L: 14s 12p 8d 6f] was used for all nonrelativistic calculations involving E126. The relativistic and NR contracted UGBS used for O were O [L: 5s 4p|S:5s 6p 6d] and O [L: 5s 4p], respectively. The contracted relativistic UGBS F [L: 5s 3p 1d|S:4s 7p 5d 1f] was used, for F while the NR contracted UGBS FNR.p-accpvdz [54] was used for the corresponding NR calculations. However for Cl, the contracted relativistic CL.accpvdz and the NR CLNR.accpvdz basis sets [54] were used in calculations on $E126Cl_6$. Our results for $E126X_6$ (X = Cl, F and O) are presented in Table 1. It should be pointed out that these are the *first* calculations for polyatomics (hexahalides and hexaoxide) of E126, however, recently we have reported in a communication our results of the *first* calculation for the diatomic E126F [60] which involves g atomic spinors in the molecular spinors of E126F. We discuss briefly the salient results of our calculation for $E126Cl_6$. The highest occupied molecular spinor (HOMS) which lies at −0.419 au for this species consists of a 60% Cl (p) and 40% E126(f) atomic spinors, whereas the lowest unoccupied molecular spinor (LUMS) (which lies at −0.0669 au) consists mostly (96%) of E126(f) atomic spinor. The atomization energy calculated with our DFNOSS relativistic wavefunction is 16.09 eV leading to a bond dissociation energy (BDE) of 2.68 eV or ∼ 62 kcal mol $^{-1}$, and so the species should be fairly stable. Moreover Mulliken population analysis [61] predicts a charge of +3.83 on E126 and −0.64 on each Cl, and the species should be highly ionic with fairly small volatility. This species would therefore be not an ideal candidate for detecting E126 in the gas phase.

Table 1 Total DFNOSS and NR Hartree–Fock (HF) energy (E) (in au) and bond length R (in Å) calculated for $E126F_6$, $E126Cl_6$ and $E126O_6$

Molecule	E (DFNOSS)	R (Å)	E (HF)	R(Å)
$E126F_6$	−67,121.8348	2.01	−54,684.6528	2.13
$E126Cl_6$	−69,289.9298	2.48	−56,845.1627	2.79
$E126O_6$	−66,973.3186	1.78	−54,536.8054	1.84

In the DFNOSS approximation, all two-electron matrix elements involving the small component of spinors are neglected only in the final SCF stage of relativistic Dirac–Fock (DF) SCF calculations. This is done in order to make the calculations manageable because the number of integrals involving small components is horrendously large even with the use of contracted basis and requires extremely large cpu time and huge disk space to store these integrals for the duration of the SCF step

10 All-electron fully relativistic coupled-cluster calculations for the open-shell atom: Rf ($6d^2$)

In order to include the relativistic as well as electron correlation effects for the superheavy atom of Rf (with the valence $6d^2$ configuration), we have performed all-electron DF as well as the corresponding NR HF coupled cluster calculations with the code [54] assuming a Gaussian nuclear model taking the atomic mass of 261 for Rf. We used our uncontracted relativistic UGBS Rf [L: 32s 32p 18d 13f |S: 32s 32p 32d 18f 13g] for all the relativistic calculations whereas the nonrelativistic uncontracted UGBS Rf [L: 32s 32p 18d 13f] was used for all the nonrelativistic calculations. Results of our NR HF as well as relativistic DF calculations are collected in Table 2. A remarkable observation from the results is that not only the calculated total nonrelativistic energy is ∼ 89% of the total DF energy of Rf., the various nonrelativistic correlation energies (MP2, CCSD, CCSD(T)) are almost the same percentage of the corresponding DF correlation energies. However, the CPU time required for the NR calculations is ∼47%. So it is much cheaper to get a reasonable good estimate of the correlation energy by performing the nonrelativistic correlation energy calculations. This would lead to tremendous saving in the computational cost of calculation of correlation energy for heavy and superheavy atoms which require huge amounts of CPU time and very large disk space for all-electron correlation energy calculations for such systems.

11 All-electron fully relativistic coupled-cluster singles doubles calculations for the closed-shell configuration of the atom of ekamercury E112

There has been considerable debate as to the chemical behavior expected of E112 the higher homolog of the well-known Hg which is a liquid. Doubts have been expressed as to whether E112 has really been synthesized or not. Since E112

Table 2 Calculated total relativistic DF and HF energy (E_{tot} in au), MP2, CCSD and CCSD(T) correlation energy (E_{corr} in au) for the open-shell 6d^{2}configuraion of Rf ($Z = 104$)

	Rf 6d^2 (DF)[a]	Rf 6d^2 (HF)[b]	Percentage[c]
E_{tot}	−38693.7919	−34,334.2540	88.7
$E_{\mathrm{corr}}^{\mathrm{MP2}}$	−3.4077	−3.00202	88.0
$E_{\mathrm{corr}}^{\mathrm{CCSD}}$	−3.2761	−2.9360	89.6
$E_{\mathrm{corr}}^{\mathrm{CCSD(T)}}$	−3.3687	−2.9956	88.9
Total CPU hours[d]	232	108	46.5

[a] All the relativistic DF calculations were performed using our uncontracted (see text) [L: 32s 32p 18d 13f|S: 32s 32p 32d 18f 13g] UGBS assuming a Gaussian nuclear model with an atomic mass of $A = 261$ for Rf (6d^2). All 104 electrons are correlated and 486 active spinors with energy up to 33,553 au are included in the coupled-cluster calculations. No such relativistic coupled cluster calculations have been reported before for Rf (6d^2)

[b] All the HF calculations were performed using our uncontracted UGBS (see text) [L: 30s 30p 18d 13f] assuming a Gaussian nuclear model with an atomic mass of $A = 261$ for Rf (6d^2). All 104 electrons are correlated and 486 active spinors with energy up to 88,914 au are included in the coupled-cluster calculations. No such nonrelativistic coupled cluster calculations have been reported before for Rf (6d^2)

[c] In this column we give the percentage of the HF value of the DF value of the quantity given in the first column

[d] On our Bugaboo cluster (96 dual 2.133 GHz Athlon processors)

Table 3 Calculated total relativistic DF and nonrelativistic HF energy (E_{tot} in au), MP2, CCSD and CCSD(T) correlation energy (E_{corr} in au) for eka-mercury ($Z = 112$) atom

	E112 (DF)[a]	E112 (HF)[b]	Percentage[c]
E_{tot}	−47,331.4142	−40,934.5532	86.5
$E_{\mathrm{corr}}^{\mathrm{MP2}}$	−3.5566	−3.0568	85.9
$E_{\mathrm{corr}}^{\mathrm{CCSD}}$	−3.4162	−2.9613	86.5
$E_{\mathrm{corr}}^{\mathrm{CCSD(T)}}$	−3.4615	−3.0027	86.7
Total CPU hours[d]	165	97	58.8

[a] All the relativistic DF calculations were performed using our uncontracted [L: 32s 32p 18d 13f| S:32s 32p 32d 18f 13g] UGBS (see text), assuming a Gaussian nuclear model with an atomic mass of $A = 277$ for ekamercury E112. All 112 electrons are correlated and 448 spinors (out of a total of 618 spinors) with energies up to 12,331 au are included in the spinor space in our coupled-cluster calculations. No such calculations have been reported for E112 ever

[b] All the HF calculations were performed using our nonrelativistic uncontracted [L:30s 30p 18d 13f] UGBS (see text), assuming a Gaussian nuclear model with an atomic mass of $A = 277$ for ekamercury E112. All 112 electrons are correlated and 464 spinors (out of a total of 602 spinors) with energies up to 37,500 au are included in the spinor space in our coupled-cluster calculations. No such calculations have been reported for E112 before

[c] In this column we give the percentage of the HF value of the DF value of the quantity given in the first column

[d] On our Bugaboo cluster (96 dual 2.133 GHz Athlon processors)

is superheavy, we would expect very pronounced effects of relativity and due to large number of electrons in its atom, electron correlation effects (considering merely the pair correlation effects) would also be very significant. We have performed all-electron fully relativistic coupled-cluster calculations for an atom of E112 using the code [54] with our uncontracted [L: 32s 32p 18d 13f|S:32s 32p 32d 18f 13g] UGBS assuming a Gaussian nuclear model with an atomic mass of $A = 277$ for ekamercury E112. All 112 electrons are correlated and 448 spinors (out of a total of 618 spinors) with energies up to 12,331 au are included in the spinor space in our coupled-cluster calculations. The corresponding nonrelativistic HF calculations were performed using our nonrelativistic uncontracted [L: 30s 30p 18d 13f] UGBS, assuming also Gaussian nuclear model with an atomic mass of $A = 277$ for E112. All 112 electrons are correlated and 464 spinors (out of a total of 602 spinors) with energies up to 37,500 au are included in the spinor space in our coupled-cluster calculations. Our results are given in Table 3. An important observation similar to that in the case of Rf discussed above is that nonrelativistic HF total energy of E112 atom is ∼87% of that of its total relativistic DF energy, and that the various nonrelativistic correlation energies are also ∼ 87% of their relativistic counterparts, and yet the nonrelativistic correlation energy calculation requires ∼ 59% of the time required for the corresponding DF calculation. It is remarkable that our nonrelativistic coupled-cluster calculations can yield $\sim 85 - 87\%$ of the DF relativistic correlation energy with substantial savings in the computational cost. Calculation of correlation energy of superheavy atoms is not a nightmare anymore.

12 Relativistic coupled-cluster calculations for the hexachloride of ekaplutonium E126Cl$_6$

The primordial superheavy element E126 ($Z = 126$) (called also ekaplutonium) has been investigated by a number of physicists [62–65] because this nucleus with a mass of 310 (with $Z = 126$) should be much more stable than any nuclide around it, since it is a doubly magic nucleus with 126 protons and 184 neutrons. As a consequence, there is a reasonable chance of observing this nuclear species and of having it persist long enough for the atoms to be isolated chemically. Recently there has been a renewed activity in the study of superheavy elements (SHE) in various laboratories [6–9]; however, at present E126 has eluded experimentalists. Theoretical investigation of superheavy element E126 and its compounds, on the other hand, should be feasible with the theoretical formalism and computational machinery available at present [15–24]. It turns out that in the ground state configuration of the atom of E126, the valence electrons occupy the g spinors (orbitals) and therefore in a molecule involving E126 there would be molecular spinors (MS) or orbitals (MO) arising from the g atomic spinor (orbital) of

Table 4 Relativistic (DF) and NR (HF) MP2, CCSD and CCSD (T) correlation energy (in au) for E126Cl_6

	DF(58e/290as)[a]	HF(68e284as)[b]
E(SCF)	−69, 289.9298	−56, 845.1627
MP2	−0.9924	−1.3191
CCSD	−1.0149	−1.1903
CCSD(T)	−1.1098	−1.4327

[a] In the DF coupled-cluster calculations, only 58 electrons were correlated and 290 spinors were included in the active spinor space of our DF coupled-cluster calculations

[b] In the HF calculations (which are cheaper than the corresponding relativistic calculations), 68 electrons were correlated and 284 active spinors (orbitals) were included in the active space of our coupled-cluster calculations

Table 5 NR (HF) MP2, CCSD and CCSD (T) correlation energy (in au) calculated with different number of electrons correlated for E126Cl_6

	HF(124e/496as)[a]	HF(80e438as)[b]
E(SCF)	−56,849.6794	−56,849.6794
MP2	−1.5089	−1.2328
CCSD	−1.6070	−1.3588
CCSD(T)	−1.7233	−1.5064
Total CPU (h)[c]	**226**	**128**

[a] In this HF coupled-cluster calculation, 124 electrons were correlated and 496 spinors were included in the active spinor space of our coupled-cluster calculations

[b] In this HF calculation, 80 electrons were correlated and 438 active spinors (orbitals) were included in the active space of our coupled-cluster calculations

[c] On our Bugaboo cluster (96 dual 2.133 GHz Athlon processors)

SHE like E126. Schrödinger's NR quantum mechanics may not be applicable in general for systems of SHE since relativistic effects are very significant for the electronic structure and bonding of systems containing superheavy elements. We have presented DF and NR HF SCF results for E126X_6 (X = F,Cl and O) molecules in the earlier Sect. 9; however, electron correlation effects which are also expected to be very significant for systems of SHE were neglected in our calculations. In this section we report our modest coupled-cluster calculations which take into account both the relativistic and electron correlation effects for E126Cl_6. Both the relativistic and nonrelativistic coupled-cluster calculations were performed assuming Gaussian nuclear model and an atomic mass of 310 for E126. The uncontracted relativistic UGBS [L: 32s 32p 18d 13f |S: 32s 32p 32d 18f 13g] contracted to [L: 14s 16p 12d 9f|S: 19s 26p 24d 18f 14g] (assuming the $6f^6$electron configuration similar to its lighter homolog Pu) was used for E126 while for Cl, the contracted relativistic basis set CL.accpvdz [54] was used for all relativistic calculations. However, for the nonrelativistic calculations (assuming the NR atomic configuration 5g6 8p2 with two open shells) involving E126, the uncontracted nonrelativistic UGBS [L: 32s 32p 18d 13f 13g] contracted to the UGBS [L: 15s 13p 10d 7f 9g] was used in all nonrelativistic calculations, whereas the uncontracted nonrelativistic UGBS [L: 18s 12p] contracted to [6s 5p] was used for Cl. The calculations were performed using the code [54] and the results are collected in Table 4.

It is well-known that the calculated correlation energy with the coupled-cluster methodology depends upon the number of electrons (n) correlated and upon the number (N) of the active spinors (orbitals) included in the active space. It is also well known that the cost of a calculation depends upon these two variables in a complicated fashion and in order to get a feeling for the cost dependence of coupled-cluster calculations upon n, we have performed two calculations with $n = 120$ and $n = 80$ while keeping the N almost the same.

The results are presented in Table 5. It is interesting that increase of n by 50% increases the cost of calculation by 80%. This may be related to the $N**X$ (where N is the number of basis functions) dependence of CCSD calculations. In addition, one has to keep also in mind that relativistic DF coupled-cluster calculation may be an order of magnitude more expensive than the corresponding NR calculation, and the cost factor is a very crucial one especially for systems of superheavy elements for which as is well known both the relativistic and electron correlation effects must be included for investigating their physics and chemistry.

13 Conclusion

In conclusion, I have shown that *ab initio* fully*relativistic* DF SCF calculations are mandatory for systems of heavy actinides and certainly for compounds of the superheavy transactinide elements. We developed the DF SCF formalism for closed and open-shell molecules 30 years ago, and we performed the first Dirac-Fock SCF calculations on the heavy diatomic gold hydride (AuH) in 1986. We have certainly come a long way during the last 2 decades and I believe not only all-electron fully relativistic DFB calculations for systems of superheavy elements with 500–600 electrons but also the RCCSD and RCCSD (T) calculations which simultaneously include both the relativistic and electron correlation effects, would be routinely performed with the supercomputer technology which would be available in the next decade.

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